Standard Operating Procedure for Analysis of Vapor Phase Mercury

Gerald J. Keeler and Matthew S. Landis
University of Michigan
Air Quality Laboratory
109 South Observatory Street
Ann Arbor, MI 48109-2029

June 1, 1994

Version 2.0

Standard Operating Procedure for Analysis of Vapor Phase Mercury

1.0 Introduction to Principals of Vapor Phase Mercury Sampling and Analysis

Mercury in the atmosphere exists predominantly in the gas phase in the form of elemental mercury (Schroeder, 1982). Other species of mercury found in the gas phase include methyl and dimethylmercury, and mercuric chloride, mercuric hydroxide and free divalent mercury. Vapor phase mercury is quantitatively removed from an air stream by amalgamation onto gold. While the amalgamation process is believed to remove most vapor phase mercury species with >99% efficiency, the analytical procedure employed determines whether or not 'total mercury' or predominantly elemental mercury is quantified. At the University of Michigan Air Quality Laboratory (UMAQL) vapor phase mercury is collected onto gold-coated borosilicate glass bead traps by drawing air at a low flow rate through a baked glass fiber pre-filter followed by the gold-coated borosilicate glass bead trap. The air is prefiltered to eliminate particles from the gas phase collection traps. After sampling, vapor phase mercury is quantified by cold vapor atomic florescence spectrometry (CVAFS).

In the past, methods for collection of vapor phase mercury have dictated long sampling duration, often from 24 hours up to a week. The collection method employed for the Lake Michigan Loading Study and described in this protocol uses gold-coated borosilicate glass bead traps, which UMAQL has determined to be >99% efficient at collection of vapor phase mercury (at a flow rate <1 lpm). Dual-amalgamation and subsequent analysis by cold-vapor atomic florescence, allows detection of mercury at picogram levels. After thermal desorption, gold-coated bead traps are reused since they do not exhibit memory effects. Due to the collection efficiency of gold-coated beads and the ability to detect picogram amounts of mercury, sampling strategies using gold-coated bead traps can employ much shorter duration samples than have previously been possible. Short sampling duration provides the resolution necessary to use receptor models in determining sources and source contributions of measured vapor phase mercury.

Preparation and collection of accurate and reliable data on mercury concentrations in environmental samples requires that ultra clean procedures are used. All sampling supplies with which a sample will come into contact must be acid cleaned in a Class 100 Clean Room. At the sampling site, precautions taken to avoid contamination of the sample include storing samples at an outdoor staging area and special operator handling. These and other techniques employed to minimize contamination of the samples are described in detail in this protocol.

2.0 Sample Preparation

2.1 Acid Cleaning Procedure

All Teflon filter packs, Teflon jars, Teflon tubing, gold trap fittings and end plugs (referred to below as 'supplies') are cleaned using an 11 day procedure described by Rossmann and Barres (1991).

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MÙ/cm)) for six hours at 80° C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for 6 hours.

After the 6 hour, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3 M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO₃ in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO₃ to 965 mL of Milli-Q water. Nitric acid is reused for up to 6 months and is stored in a carboy dedicated for HNO₃. At the end of the 3 day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56 M Baker Instra-Analyzed HNO₃ that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for 7 days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO₃ to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

2.2 Preparation of Gold-Coated Bead Traps and Pre-Filters

Gold-coated borosilicate glass bead traps are constructed at The University of Michigan Air Quality Laboratory and tested prior to use in the field. The gold-coated beads used in the traps are made by generating a gold plasma under vacuum conditions that uniformly deposits onto the surface of the beads. The thickness of the coating generated using this process is about 300 Å. The gold-coated beads are contained in a quartz tube which is 10 cm long with an inner diameter of 5 mm and an outer diameter of 7 mm. Teflon heat-shrink tubing is attached to both ends of the tube into which Teflon endplugs are placed when the trap is in storage or connectors when the trap is being used to collect a sample. Each trap contains approximately 0.7 g of gold-coated borosilicate glass beads which are held in place using quartz wool and two sets of three radial indentations in the quartz tube. The gold-coated beads, quartz tubes and quartz wool are baked at 600°C for one hour prior to making the trap. In addition, Teflon endplugs and heat shrink tubing are acid cleaned as previously described. After each trap is made, it is given a unique number identifier in order to chart the history and performance of the trap. New traps are first conditioned by drawing approximately 0.4 m³ of air through the trap then heating the trap to 500°C for 5 minutes. Inert gas is purged through the traps at 300 cc/min during heating procedure to remove

moisture and other volatile constituents. The conditioning procedure is performed twice prior to testing the trap. The trap is then tested by injecting a known amount of elemental mercury vapor and comparing the result to an analytical standard (standard generation is described on page 9). The trap must exhibit duplicate measurements that are within 5% of the standard and the replicate measurements must also be within 5% of each other. Following this test, the trap is then blanked (described below) and stored for 7 days. After 7 days, the trap is analyzed for a storage blank (sample analysis is described in Section 3.0). The storage blank must be less than 15 pg for the trap to be accepted for use in field sampling. Gold traps are stored with endplugs in place, triple bagged in polyethylene before and after sampling.

Just before going into the field to collect vapor phase mercury samples, gold-coated bead traps are blanked again. Blanking a trap removes all mercury from the gold-coated bead surface and will also remove water vapor and other unwanted constituents. Traps are blanked by placing them in the analytical train and heating them to 500°C for 2 minutes, identical to a normal sample analysis.

Vapor phase mercury samples collected onto gold-coated borosilicate glass bead traps must be prefiltered to exclude particles. Glass fiber filters (Gelman Sciences) are pre-treated to remove all mercury prior to use in sampling. Glass fiber filters, 47 mm in diameter, are placed in a clean crucible with a lid. The crucible is placed in a muffle furnace which is heated to 500°C and the filters are allowed to bake at this temperature for one hour. While hot, filters are removed from the crucible with acid-cleaned Teflon-coated forceps and placed in an acid-cleaned Teflon jar which is closed and sealed with Teflon tape. The Teflon jar is triple bagged and stored at -40°C until use. Filters are stored no more than 3 months prior to use and frequent blanks are taken to ensure the filters remain clean.

3.0 Sample Analysis

3.1 Summary

Vapor phase mercury collected onto a gold-coated bead trap is thermally desorbed and carried by a mercury-free helium stream into a cold-vapor atomic fluorescence (CVAFS) analyzer where the mercury atoms are excited by light of wavelength 253.7 nm. These excited atoms fluoresce in the same wavelength which is detected by a photomultiplier tube and the signal is converted to voltage which is sent to an integrator.

Gold-coated bead traps are >99% efficient at collecting mercury in its various forms in the atmosphere. In sampling locations away from local sources the predominant form of mercury in the atmosphere is elemental mercury, however, in source regions, there may be an important fraction of other mercury species present. The temperature used to desorb mercury from the traps determines whether or not a mercury compound (other than elemental mercury) released from the gold is in elemental form or a molecular form. Typically, when gold-coated bead traps are employed, a desorption temperature of 500° C or less is used since the melting point of borosilicate glass is typically about 650° C (rendering the trap unusable). At 500° C mercury compounds will not quantitatively be converted into elemental mercury. Published values for temperatures required to break methyl mercury bonds approach 1000° C. Therefore, in environments in which there may be mercury species other than elemental mercury, in the atmosphere, it is incorrect to term this CVAFS procedure an analysis of "total gaseous phase mercury". At UMAQL a desorption

temperature of 500° C is employed and results of this analysis are referred to simply as "vapor phase mercury".

3.2 Sample Analysis and Data Acquisition

The CVAFS analyzer used for vapor phase mercury analysis is operated in a normal laboratory setting (outside of the clean room) because the risk of contamination of the samples is minimal. The instrument is keep on at all times, since this has been shown to stabilize the UV lamp and maintain consistency from one day to the next. The power supplied to the CVAFS analyzer is modulated by a line tamer (Shape Magnetronics) to prevent power fluctuations. It is imperative that the mercury lamp not experience wide temperature fluctuations or power surges since both of these drastically affect the sensitivity of the instrument. During operation of the instrument the helium carrier gas flow rate is regulated upstream of the analyzer using a mass flow controller (Tylan) which is set to maintain a 35 cc/min flow rate. This flow rate has been determined by UMAQL to yield the optimal peak characteristics for mercury standards. The regulator on the helium cylinder is set at 50 Kilopascals. The helium stream is prefiltered using a gold-coated trap before entering the analytical train in order to remove any mercury. In the analytical train, mercury is thermally desorbed from the sample trap, and amalgamated onto the analytical trap which is subsequently thermally desorbed into the CVAFS analyzer where the mercury atoms are detected. Traps are desorbed by heating a nichrome coil which is wrapped around the trap covering the gold-coated beads. Application of 12 volts of current to the coil is sufficient to achieve a temperature of 500° C inside the gold bead trap (voltage may vary due to variations in length and thickness of nichrome wire). Two fans supply cool air to the sample and analytical trap separately in order to speed analysis time.

For comparability between laboratories UMAQL sets the gain on the CVAFS analyzer to yield an approximate 1000 mV net response for a 1 ng mercury standard. The background on the CVAFS analyzer is set at 5.0 and maintained in that position in order to track the drift in the baseline of the analyzer. A Hewlett Packard Integrator is connected to the analyzer to convert output signal into an integrated area of the detected response. Area units are used for all sample calculations since area is much more reliable than peak height.

Particle-free clean room gloves are worn during all procedures. To analyze a sample trap, the trap is placed snugly into the analytical train using friction fit Teflon connectors and Teflon sleeves. The nichrome coil used specifically for the sample trap is slid over the trap and moved to completely cover the quartz wool plugs and the gold-coated beads contained between the plugs. Helium is allowed to flow through the sample trap for 2 minutes before analysis begins in order to purge air and water vapor from the analytical train. A circuit controller (ChonTrol) is employed which is programmed to turn on the variable transformers and fans in a precise and reproducible manner. First, the sample coil is heated for 2 minutes, then it is cooled while the analytical trap is heated for 2 minutes. The analytical trap is then cooled for 2.5 minutes and the fan to the sample trap is turned off. While the analytical trap is cooling, a new sample trap is installed in the analytical train and helium is passed through this trap until the analytical trap is cool and ready for another sample. When the analytical trap begins heating, the integrator is turned on and the ambient temperature, time and base mV are recorded in a log book and the LCD display on the analyzer is set to record the peak mV (by depressing the Peak button on the face of the analyzer). After the sample is analyzed and the peak height and area reported by the CVAFS and integrator respectively, these values are recorded in the log book.

A standard curve is analyzed at the beginning of each day of analysis and a control standard which yields a response in the range of the samples being analyzed is run every six samples. Criteria for the standard curves and control standards are described below in Section 3.3. All sample analysis is recorded in a log book specific to the analyzer with which samples are being quantified and also in a lab notebook specific to the study for which the samples were collected. At the end of the day of analysis all results from the log sheet are entered into an Excel spreadsheet for subsequent checking and processing by a statistical software program, SAS (Cary, NC).

3.3 Standard Curve and Control Standards

A standard curve, generated by injecting different volumes of mercury saturated air, is analyzed before each day of analysis. The amount of mercury per volume of mercury saturated air depends on the temperature of the mercury saturated air. This relationship is described by the Ideal Gas Law. The amount of mercury injected for the calibration curve is tailored to the expected value of the samples to be analyzed. At UMAQL, a typical calibration curve consists of five injection volumes: 0 mL, 20 mL, 40 mL, 80 mL and 160 mL of mercury saturated air, which represent mercury masses shown in Table 1.

Standards for the calibration curve are generated by withdrawing known volumes of gaseous elemental mercury from the headspace of a closed 150 mL flask containing about 2-3 mL of metallic mercury. The flask is maintained below ambient temperature by being immersed in a constant temperature (+\- 0.1° C) circulating water bath. The temperature of the circulating water bath and thus the flask of mercury saturated air is usually maintained at a temperature of 16.6° C while ambient temperature is about 22-24° C. The temperature of the flask must be maintained below ambient temperature otherwise, the mercury injected will condense on the walls of the injection apparatus. Also, the flask is purged periodically with N_2 in order to displace oxygen which may oxidize the surface of the mercury. The mercury is withdrawn from the flask using a gas tight syringe (Hamilton) and is injected onto and quantitatively captured by a gold coated bead trap. The trap is then thermally desorbed and analyzed using the CVAFS analyzer.

At the start of each day of analysis, the syringe is "conditioned" for 15 minutes. The syringe is conditioned by flushing it three times with mercury saturated air, then the maximum amount of mercury saturated air is pulled into the syringe and the needle is left inside the flask for 15 minutes. While the syringe is conditioning, the injection port is inserted into the analytical train and is connected to a gold coated bead test trap using friction fit Teflon connectors. The injection port is fitted with a Minnert valve and Teflon coated silicon septum. After 15 minutes, the syringe is flushed with mercury saturated air three times and 80 mL is withdrawn and injected onto the test trap to "condition" the injection port. The injection port is conditioned for a total of three times before the syringe and injection port are ready to be used for a calibration curve. This conditioning process is necessary before each day of analysis to ensure precise and reproducible results.

The standard curve is generated starting with the zero point (0 mL) and continued in ascending order to the highest volume, usually 160 mL. First, a blanked gold-coated bead trap is attached to the downstream end of the injection port. Prior to withdrawing the necessary volume of mercury saturated air for each injection, the temperature of the flask is recorded and the syringe is flushed three times with mercury saturated air. After flushing the syringe, the required volume of mercury saturated air is withdrawn. The syringe is then removed from the flask and the mercury saturated air is injected onto the gold trap via the injection port as quickly as possible to avoid diffusion of

mercury from the needle tip. After the injection is complete, the syringe is returned to the flask and the maximum amount of mercury saturated air is pulled into the syringe and allowed to sit until the next injection. After the trap is loaded with a standard amount of mercury, the injection port is removed from the analytical train and the trap is analyzed as described above. The injection port is kept sealed in a polyethylene bag between injections.

The zero point of the calibration curve (0 mL) is generated in the same manner described above except that no mercury saturated air is withdrawn into the syringe. Instead, the syringe is flushed three times and fully depressed prior to removing the syringe from the flask and the needle is promptly inserted and removed from the injection port. The zero point indicates the amount of mercury that comes from the needle tip and the injection apparatus and is usually between 1-6 pg. The 0 mL injection is also a good indication of when the septum in the injection port needs to be changed. If the 0 mL injection is higher than 10 pg then the septum is changed. Otherwise, the septum is changed after loading 30 traps for standards or controls.

At any given temperature the vapor density of mercury can be calculated using the Ideal Gas Law and the saturation vapor pressure of mercury. A table of associated vapor densities versus temperature has been compiled and is used to determine the amount of mercury injected for each standard. Table 1 lists the amount of mercury delivered for the 5 injection volumes used to generate the standard curve at a temperature of 16.6° C.

Table 1. Amount of Mercury Injected for a Typical Calibration Curve

Volume of Mercury Saturated Air Injected (mL)	Amount of Mercury Injected (ng)	
0	0	
20	0.198	
40	0.396	
80	0.793	
120	1.190	

Flask temperature = $16.6^{\circ}C$ Vapor density = 9.912 ng/cm^3 $1 \text{ cm}^3 = 1000 \text{ mL}$

After the standards for the calibration curve have been analyzed, a linear regression is calculated to establish the coefficient of determination (r^2) , the slope of the line and how well the slope of the curve predicts each of the points in the calibration curve. The slope of the line is forced through

zero and the 0 mL injection area is subtracted from each of the points on the curve. The r^2 must be >0.999 and each of the points on the curve must be predicted by the slope within 5% of their true value (Table 2). If these criteria are not met, specific points which are errant are repeated and the linear regression recalculated.

Standard (ng Hg)	Response Area Units	Response - Zero Point	Predicted Value (ng Hg)
0	71,219	0	0
0.198	2,286,400	2,215,181	0.197
0.396	4,495,200	4,423,981	0.393
0.793	9,089,300	8,946,862	0.794
1.190	13,597,000	13,383,343	1.190

Table 2. Example Calibration Curve and Calculation of Slope:

Slope = 8.8886E-8 ng/AU Slope⁻¹ = 11,250,357 AU/ng $r^2 = 0.9999$

This curve is accepted and sample analysis commences.

Control standards are analyzed every sixth sample. The control standards are generated in the same manner as described above and are chosen to be representative of the samples being analyzed, usually an 80 mL injection. The integrated area from each of the control standards must be within 5% of the slope of the calibration curve in order to continue analyzing. If this is not the case, a second control is analyzed immediately. If the second control indicates that analyzer sensitivity has changed a second calibration curve is generated and sample analysis is continued.

The mercury flask is checked weekly to determine if the surface of the mercury is oxidized. If there is visible discoloration on the surface of the mercury then the flask is purged for 15 minutes with N_2 to reduce the oxidized layer. Also, to determine if water has entered the flask the mercury is gently swirled around the bottom of the flask. If the mercury moves around the flask without adhesion to the glass then there is no water in the flask.

3.4 Calculation of Mercury Concentration in Sample

The vapor phase mercury concentration from a set of gold-coated bead traps is calculated in ng/m³. First, the amount of mercury detected on each of the sample traps (A & B) is calculated by multiplying the integrator response from the individual trap by the slope of the calibration curve which is in ng/Area Unit (AU). The product is ng of mercury (Table 3). Each trap is field blank corrected and the results are summed to yield the total mercury mass collected. The calculated value, in nanograms of mercury is converted to ng Hg/m³ by calculating the total volume of air drawn through the sample and dividing the ng of mercury by the cubic meters of air sampled.

Table 3. Calculation of ng Hg/m³ in a Vapor Phase Sample.

1. Calculation of ng of mercury recovered from a set of sample traps

ng Hg on the Sample Trap (A) = Response (AU) x Slope of the calibration curve (ng/AU) $7,135,900 \ x$ 8.8886E -8 = 0.634 ng Hg

ng Hg on the Sample Trap (B) = Response (AU) x Slope of the calibration curve (ng/AU) $281,560 \ x \ 8.8886E - 8 = 0.025 \ ng \ Hg$

2. Field blank correction and summation of traps Corrected ng Hg on Sample Traps = (ng on trap A + ng on trap B) - 2(mean ng of field blanks) (0.634 + 0.025) - 2(0.016) = 0.627

3. Calculation of m³ sampled at a flow rate of 300 cc/min and a sample duration of 24 hours:

Flow Rate x Duration of Sample = Volume of Air Sampled

$$\frac{300ml}{\min} \times 24 \ hr \times \frac{1,440 \ \min}{24 \ hr} \times \frac{m^3}{1,000,000 \ ml} = 0.432 \ m^3$$

4. Concentration of Vapor Phase Mercury in Sample = ng Hg/m³

$$\frac{0.627 \text{ ng Hg}}{0.432 \, m^3} = 1.451 \, \text{ng Hg} / m^3$$

3.5 Trouble-Shooting

A source of irreproducible results may be due to faulty gold-coated bead traps. These traps are numbered with discrete identifiers. All samples must be identified with a particular trap number and trap performance must be tracked. Contact with halogen fumes, organic fumes or overheating of the trap during analysis can damage the trap, rendering it unusable. If performance of a gold trap is suspect, at least two consecutive standards are analyzed from this trap to determine its ability to amalgamate and release mercury.

Another source of irreproducible results could be from water or water vapor seeping into the flask containing mercury. If this is the case, the mercury in the flask is properly discarded and the flask is rinsed with $0.56M\ HNO_3$ and allowed to thoroughly dry. After drying, the flask is replenished with about 2-3 mL of triple distilled metallic mercury and purged with clean N_2 for 5 minutes. The flask is then be returned to the constant temperature water bath and allowed to thermally equilibrate and to reach saturation for at least 3 hours.

If a low response is observed, the trap loading apparatus is checked for leaks, especially the plunger tip in the syringe or the where the needle contacts the plunger tip. If the plunger tip is worn, the syringe will no longer be gas tight and needs to be carefully replaced without damaging the plunger tip. If there is any material (Teflon shavings, etc.) in the base of the needle where it contacts the plunger tip, the material is wiped away with a particle-free clean wipe. Also, the side port hole in the needle tip is checked to make sure that it is not clogged with any foreign material (Teflon from the septum, etc.).

If peak-broadening is observed or no peak is detected in a sample, the analytical train is checked for leaks. Peak broadening is often the result of low gas flow, water vapor on the gold-coated bead trap, inadequate heating of analytical trap or an analytical trap damaged by exposure to halogen fumes or overheating. Analytical traps are replaced only when a potential problem is suspected with the trap.

If a broad peak is observed directly after the sharp mercury peak then the problem is most likely a thermally or chemically damaged trap and the line from the analytical trap to the detector is replaced as gold atoms may have been liberated from the trap and migrated down stream.

If the baseline drifts more than 10% the UV lamp is replaced. After replacement, the analyzer is allowed to equilibrate for 24 hours. If the problem persists, sources of power fluctuation, drafts or air currents that may be changing the temperature of the UV lamp are investigated.

Room temperature in which the CVAFS is located is maintained between 20-22°C, however, if the temperature exceeds 26° C analysis is stopped, since instrumental noise increases significantly.

4.0 Performance Criteria, Quality Assurance and Quality Control

- 4.1 Field operators are carefully instructed in the techniques of contaminant-free vapor phase mercury collection. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network.
- 4.2 Every 6 months UMAQL personnel will inspect the sampling sites to audit the sampling equipment and make all necessary repairs or adjustments.
- 4.3 Co-located samples are collected from one sampling site during the study to quantify method precision. Reported concentrations are based on the mean of the two co-located samples.
- 4.4 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 10% is maintained for samples with values at least 3 standard deviations greater than the detection limit. Analysis of standards and controls is within 5% of the stated value.
- 4.5 A minimum of 25% of all samples analyzed are field blanks or analytical blanks to ensure that samples are collected in a contaminant-free manner.
- 4.6 Every 3 months maintenance on the CVAFS analyzer is conducted, including replacement of the

- UV lamp, the Teflon tubing, and the detection cell.
- 4.7 Gold traps are checked prior to every sample with 0.8 ng of mercury in order to ensure that their use during the previous sample collection has not diminished trap performance.

5.0 References

- 5.1 Bloom, N.S. and Fitzgerald, W.F. (1988) Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. *Anal. Chem. Acta.* 208, 151.
- 5.2 Dumarey, R., Temmerman, E., Dams, R. and Hoste, J. (1985) The Accuracy of the Vapour-Injection Calibration of Mercury by Amalgamation/Cold-Vapour Atomic Absorption Spectrometry. *Anal. Chem.*. *Acta*. 170, 337-340.
- 5.3 Dumarey, R., Dams, R., and Hoste, J. (1985) Comparison of the collection and desorption efficiency of activated charcoal, silver, and gold for the determination of vapor-phase atmospheric mercury. *Anal. Chem.* 57, 2638-2643.
- 5.4 Fitzgerald, W.F., and Gill, G.A. (1979) Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. *Anal. Chem.* 15, 1714.
- 5.5 Lindberg, S.E. (1981) Author's Reply 'Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms.' Atmos. Environ. 15, 631-635.
- Rossmann, R. and Barres, J. (1991) Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage, and analysis *J. Great Lakes Res.* 14,:188.
- 5.7 Schroeder, W.H. (1982) Sampling and analysis of mercury and its compounds in the atmosphere. *Environ. Sci.. Technol.* 16, 394-400.

APPENDIX A: FACILITIES, EQUIPMENT AND REAGENTS

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation, sample collection and sample analysis that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

- Class 100 Clean Room, Work Stations
- Clean Room Gloves
- Particle-free Wipes
- Clean Room Cap, Gown and Boots
- Milli-O Water (18.2MÙ/cm)
- Exhaust Hood
- Acetone
- Alconox
- Polyethylene Tubs
- EM Science Tracepur and Suprapur Hydrochloric Acid
- Polytherm Water Bath (Science/Electronics)
- Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
- New Polyethylene Bags
- 20 Liter Polyethylene Carboys

2. Sample Collection

- Mass Flow Controlled Vacuum Pump (URG, Model 3000-02M)
- Calibrated 300 cc/min Rotameter (Matheson)
- HDPE Tubing with quick connects
- Black Latex Tubing
- Mercury Sampling Box (UMAQL, See Appendix B)
- Acid-Cleaned 47 mm Teflon Filter Holders (Savillex, PFA Labware)
- 47 mm Preheated Glass Fiber Filters (Gelman Sciences A/E)
- Acid-Cleaned Teflon Jars (Savillex, PFA Labware)
- Teflon-Coated Forceps
- 'Blanked' Gold-Bead Traps (UMAQL)
- Teflon Endplugs
- Trap Heater & Variable Transformer
- Acid-Cleaned Teflon Tubing
- Particle-Free Gloves
- Teflon Tape
- Sample Labels
- Field Operator Log Book
- Shipping Boxes

3. Sample Analysis

- Cold Vapor Atomic Florescence Detector (Brooks Rand, LTD.)
- Line Tamer/Conditioner (Shape Magnetronics Model PCLT 150)
- Integrator (Hewlett-Packard Model 3390A)
- Helium, Ultra High Purity Grade (99.999%)
- Mass Flow Controller (Tylan)
- Nichrome Coils (UMAQL)
- Electric Leads
- Variable Transformers (Staco Energy Products Co. Type 3PN1010)
- Cooling Fans
- Gold-Coated Glass Bead Traps (UMAQL)
- Gas Tight Syringe (Hamilton series 1800)
- Injection Port (UMAQL)
- Constant Temperature Circulating Water Bath (Fisher Model 901)
- Instrument Grade Metallic Mercury (Triple Distilled)
- Mercury Flask (UMAQL)
- Certified Immersion Thermometer (Kessler Instruments, Inc. 15041A)